

General Aspects in Polymer Synthesis

by H. K. Reimschuessel*

The term, synthetic polymer, denotes a macromolecule composed of simple structural units and usually derived from monomers by a process of polymerization. This process is possible only if certain chemical, thermodynamical, and mechanistic conditions are satisfied. The monomer must have a functionality of two or higher. The polymerization process must be characterized by a negative free energy change. The monomer must have activable or reactive functions. Activable structures are polarizable multiple bonds, and bonds entailing heteroatoms in ring compounds. Suitable reactive functions are those that participate in: carbonyl addition, substitution, multiple bond addition, and free-radical coupling. According to their growth mechanisms, polymerization reactions are divided into two major groups: chain-growth polymerization and step-growth polymerization. Polyaddition and polycondensation occur in either group, but polyinsertion is a chain-growth process exclusively. Radical, ionic, and heterogeneous initiations are entailed in chain growth, whereas both nucleophilic and electrophilic initiation prevails in step-growth. The chemical structure of polymers is determined mainly by constitutional and configuration parameters. Principal constitutional ones are related to interlinking of chains and structural units, composition, substituents, endgroups, and the molecular weight. Configurational ones refer particularly to the position of substituents on a central chain atom relative to the neighboring structural unit and thus to the tacticity of the polymer.

The term, "synthetic polymer" denotes a macromolecule that is constructed from sequences of simple structural units, and is usually derived from monomers by a process of polymerization. The structural units may either be all identical or belong to classes of different types. In the former case, the polymer is known as a homopolymer; in the latter, it is called a copolymer. In either case, any process of converting monomers into a polymeric structure will proceed only if certain chemical, thermodynamical, and mechanistic conditions are satisfied. They are (chemical) a functionality of the monomer of two or higher; (thermodynamical) a negative change in the free energy according to $\Delta G_{MP} = \Delta H - T\Delta S < 0$; (mechanistic) a potential for activation of the monomer and a high rate of polymerization in comparison to the sum of the rates of all other possible reactions.

The functionality is no intrinsic property of a particular monomer but depends upon the reaction partner or the mode of reaction. The effective functionality may therefore be higher or lower than the monomer formula functionality. For instance, a 1,6-diene has a formula functionality of four; it does, however, undergo intramolecular cyclization which results in the formation of difunctional structural units. Thus the effective functionality is two. On the other hand, with respect to radical initiation the C=C double bond in vinyl chloride has a functionality of two. Radicals are capable of abstracting a chlorine atom from a polyvinyl molecule, thereby generating a polymer radical which in turn may initiate additional polymerization of vinyl chloride. The effective functionality in this case is therefore higher than the formula functionality.

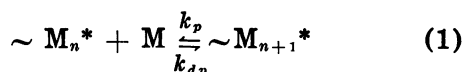
Whereas the isocyanate group is difunctional with respect to anionic initiation, it has less than the equivalent functionality with respect

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to hydroxyl groups because of allophanate formation entailing the initially formed urethane groups. Thermodynamically, polymerization is feasible if ΔG_{MP} is negative. This is realized in three of the four special cases shown in Table 1.

Independent of the particular mechanism and the natures of both the initiating and the propagating species, polymerization reactions are generally governed by any or all of three principal equilibria: monomer-chain; chain-chain; and chain-ring.

The monomer-chain equilibrium can be represented by the simple reaction (1):



from which follows eq. (2).

$$K_n = \frac{[\sim M_{n+1}^*]_e}{([M]_e [\sim M_n^*]_e)} \quad (2)$$

Table 1. Thermodynamic feasibility of polymerization.

$$\Delta G_{MP} = \Delta H_{MP} - T\Delta S_{MP} \simeq -RT \ln K_n$$

Case	ΔH_{MP}	ΔS_{MP}	ΔG_{MP}	Polymerization
I	-	+	-	Possible; examples unknown
II	+	-	+	Impossible at any temperature
III	-	-	(for $\bar{T} < T_c$)	Possible at $T < T_c$ (T_c = ceiling temperature)
IV	+	+	(for $\bar{T} > T_i$)	Possible (S_i, S_c) at $T > T_i$ (T_i = floor temperature)

For M_n approaching infinity, $n+1 \sim n$, and thus $K_n = 1/[M]_e$.

The equilibrium concentration $[M]_e$ depends upon the constitution of the particular monomers. Table 2 shows the equilibrium monomer content for some polymers derived from vinyl monomers. Table 3 contains values for $[M]_e$ for the lactam-derived polyamides.

Chain-chain equilibria are usually encountered in polymers containing heteroatoms (polyesters, polyamides, polyurethanes, polysiloxanes) as a result of exchange and re-equilibration reactions. These reactions are

Table 2. Equilibrium monomer content at 25° C.

Monomer	$[M]_e$, mole/l.
Vinyl acetate	10^{-3}
Styrene	10^{-6}
Methyl methacrylate	10^{-3}
α -Methylstyrene	2.8

Table 3. Monomer-polymer equilibrium concentrations for substituted lactams.

Lactam	Ring substituent	Lactam present at equilibrium, wt-%
Caprolactam	None	7
	5-Methyl	8.8
	7-Methyl	9.5
	5-Ethyl	30.2
	5-Propyl	41
	5-Isopropyl	37
Enantholactam	5- <i>tert</i> -Butyl	74
	None	0
	8-Ethyl	3
	8- <i>n</i> -Propyl	6
	N-Methyl	20


characterized by no change in the reaction enthalpy.

Ring-chain equilibria are generally a consequence of the competition between the intermolecular reaction of polymerization and the intramolecular reaction of cyclization, the extent of which depends upon constitutional and conformational factors.

The third prerequisite pertains to the potential of the monomeric species for their activation. This presupposes the presence of activable structures and/or reactive functions. Structures that are readily activated are polarizable multiple bonds, and bonds entailing heteroatoms in ring compounds. The former include carbon-carbon double and triple bonds, carbon-oxygen double bonds, and carbon-nitrogen triple bonds; the latter are found in compounds such as cyclic ethers, lactams, lactones, and cyclic siloxanes. Reactive functions suitable for polymerization reactions are the functional groups generally entailed in: (1) carbonyl addition reactions, (2) substitution reactions, (3) multiple bond addition reactions, and (4) free-radical coupling reactions.

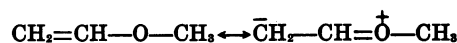
Some of these groups and the corresponding polymerization products are listed in Table 4 for the particular types of reactions.

Table 4. Activable structures and reactive functions.

Polarizable multiple bonds $(\text{C}=\text{C}; \text{C}=\text{O}; \text{C}\equiv\text{C}; \text{C}\equiv\text{N})$ σ Bonds entailing heteroatoms in ring compounds (cyclic ethers, lactams, lactons, cyclic siloxans)	$\text{A}=\text{B}\rightarrow-\text{A}-\text{B}-$ $\left(\begin{array}{c} \text{X} \\ \\ \text{C}^2 \end{array}\right)\rightarrow-\text{X}-\text{C}^2-$
Functions entailed in Carbonyl additions Elimination (O^- ; OH ; NH_2 ; COO^-) Substitution (ArH ; OH)	Polyesters, polyamides polyimides Polyacetals, phenol, urea, melamine resins
Substitution Nucleophilic (halide; sulfide; epoxide; OH) Electrophilic (halide; SO_2Cl ; COCl)	Epoxy resins, polyethers polythioethers Polybenzyl, poly(<i>p</i> -phenylene), polysulfones, polyketones
Multiple bond addition $(-\text{N}=\text{C}=\text{O}; -\text{C}=\text{C}-;$ $-\text{C}\equiv\text{C}-; \text{O}=\text{C}=\text{C}=\text{C}=\text{O};$ $\text{N}=\text{C}=\text{O}; \text{OH}; \text{SH}; \text{NH}_2;$  ; SiH ; SnH)	Polyurethanes, polysulfides, Diels-Alder polymers, polycarbodiimides, organometallic polymers; polyethers, polyesters, polyamides.
Free-radical coupling reactions $(\text{OH}; -\text{C}\equiv\text{CH}; -\text{C}(\text{R}_2)\text{H}; \text{SH})$	Polyethers (thioethers), polyacetylenes, poly(phenylene isopropylidene)

The activation of multiple bonds depends on certain factors, the principal ones being extent of polarization, structure (steric factors), and extent of resonance stabilization. Since the contribution of any of these factors to the activation of multiple bonds can vary considerably from one monomer to another, the response to particular initiators may thus be quite different for different monomers. For instance, the polymerization of styrene can be initiated by radicals, cations, anions and complex initiators (Ziegler catalysts), vinyl esters polymerize only by radical initiation whereas vinyl ethers cannot be polymerized by radicals; formaldehyde can be polymerized both cationically and anionically, but acetaldehyde polymerizes only upon cationic initiation. The extent of polarization is about the same for both aldehydes ($-\text{C}^{\delta+}=\text{O}^{\delta-}$) making them both susceptible to an attack by either an anion or cation; however the carbon atom in the acetaldehyde is shielded by a methyl group which prevents the approach of an anion. Polarization of the carbon-carbon

double bond results from the electron-donating or electron-accepting characteristics of substituents. Examples are acrylic esters and olefins such as propylene and isobutylene. The electron-withdrawing ester group is responsible for a partially positive charge at the carbon of the $=\text{CH}_2$ group, whereas a partially negative charge at this group in case of the two olefins results from the electron donating characteristics of the methyl groups. Thus anions will initiate the polymerization of acrylic esters, but not that of propylene or isobutylene, cations on the other hand will initiate polymerization of these olefins but not of acrylic esters. An attack on the carbon atoms carrying the substituents is in the considered cases for steric reasons not possible. Vinyl ethers are cases where initiation by radicals is not possible because of resonance stabilization:

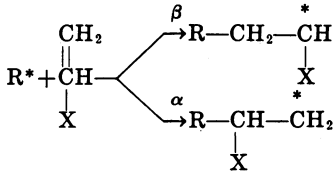

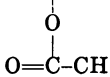


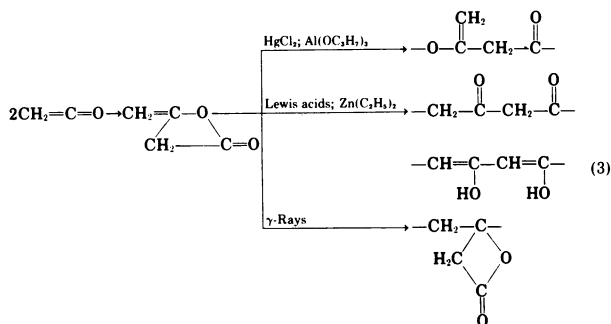
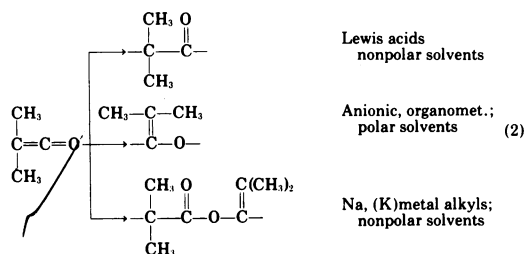
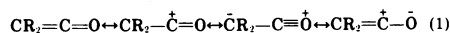
These compounds can be polymerized by cationic initiation.

Factors affecting the activation of the double bond determine also the position of attack. They determine thus to a large extent the chemical structure of the polymer. Steric parameters, resonance stabilization, and intramolecular interaction determine (Table 5) the extent to which 1:1 (head-to-head) addition occurs.

Depending upon the initiator system, polymers of different chemical structures may be derived from monomers characterized by more

Table 5. Position of attack.

		
X	α , %	
	0	Steric hindrance at αC ; polystyryl radical resonance stabilized
	2	Dipole-dipole interaction entailing COO groups in the transition state
-F	30	Small size of substituent



than one activable double bond. Examples are shown for ketenes in eqs. (1)–(3).

The types of initiation employed for some well known monomers are shown in Table 6. Some of the most commonly used initiator systems are summarized in Table 7.

The ability of many monomers to polymerize by more than one mechanism (which may—as shown for the ketenes—result in different polymer structures) makes it often difficult to identify the mechanism by which a particular polymerization proceeds. The type of mechanism that governs a polymerization process can not always be derived from the initiator system

employed. For instance, components of Ziegler catalysts such as aluminum alkyls and titanium chlorides initiate by themselves anionic and cationic chain reactions, respectively. A system of the triisopropoxides of aluminum and phenyltitanium initiates radical polymerization of styrene. Boron compounds are used in both radical and cationic initiation. Iodine initiates the cationic polymerization of vinyl ethers, but in complexes with benzene or dioxane it initiates the anionic polymerization of certain monomers. For this reason additional criteria have been considered for the identification of the actual mechanism. Among them are tem-

Table 6. Initiation mechanisms for different monomers.

Monomer	Initiation mechanism ^a			
	Radical	Anionic	Cationic	Metal complex
Ethylene	$\text{CH}_2=\text{CH}_2$	⊕	+	⊕
Propylene	$\text{CH}_2=\text{CH}-\text{CH}_3$		+	⊕
Butene-1	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$			⊕
Isobutene	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_3$		⊕	+
Butadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	⊕	+	⊕
Isoprene	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$	+	+	⊕
Styrene	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	⊕	+	+
Vinyl chloride	$\text{CH}_2=\text{CHCl}$	⊕		+
Vinyl ethers	$\text{CH}_2=\text{CHOR}$		⊕	+
Acrylates	$\text{CH}_2=\text{CH}-\text{COOR}$	⊕		

^a + denotes possible initiation; ⊕ denotes industrial process.

Table 7. Initiator systems.

Radical	Ionic		Heterogeneous	Pseudoionic	
	Anionic	Cationic		Anionic	Cationic
Peroxides	Bases	Protonic acids	$(C_2H_5)_3Al/TiCl_4$	Li organic Na phenolate	$HClO_4$
Persulfates	Alkali metals	Lewis acids	$(C_2H_5)_2AlCl/TiCl_3$		CF_3COOH
Hydroperoxides	Alcoholates	I_2 , $tBuClO_4$	$LiAlR_4/TiCl_4$		
Azo compounds	Metal ketyls	Ph_3CCl	$Al(C_2H_5)_3/VCl_3$		
Organoboron compounds	Phosphine	Acyl perchlorate	$Al(C_2H_5)_3/TiI_4$		
Metal peroxides	Grignard compounds		Metal oxides Metal salts Metal alcoholates		

Table 8. Criteria for identification of reaction mechanism.

Temperature dependency of reaction rate	(inadequate)
Solvent effects	
Radical:	independent of dielectric constant of solvent
Ionic:	proceed well in polar solvents
Insertion:	require nonpolar solvents
Effect of additives	
Alkyl halides:	not anionic ($RMe^+ + R^1Cl \rightarrow R-R^1 + MeCl$)
Diphenylpicrylhydrazyl:	stops radical reaction but not ionic reaction
$CH_3OT: \sim M^- + CH_3OT \rightarrow \sim MT + \overline{O}CH_3$	
$^{14}CH_3OH: \sim M^+ + ^{14}CH_3OH \rightarrow \sim M - O^{14}CH_3 + H^+$	
Water:	does not affect pseudocationic reaction but stops cationic reaction
Copolymerization	

perature, type of solvent, presence of both additives and comonomers. Some of the criteria for identifying the reaction mechanism are listed in Table 8.

The use of comonomers for identifying the mechanism of a particular polymerization process is demonstrated in Table 9.

Polymerization Mechanisms

Classically, polymerization reactions have been divided into two major groups: polyaddition and polycondensation. Although still widely

used, this classification does not accommodate adequately the mechanistic aspects of all the polymerization processes known to date. A more appropriate system is based upon the general growth reaction mechanisms entailed in polymerization processes. It consists of two main classifications, which are chain-growth polymerization and step-growth polymerization. The former pertains to a reaction in which a polymer chain, once initiated, grows rapidly to its final degree of polymerization and becomes incapable of further growth from either end upon termination. Both prior to and after termination the polymer chain is generally also incapable of reacting with other polymer chains. The principal steps in this polymerization reaction are the processes of initiation, propagation, and termination. Each of these processes is generally characterized by a specific mechanism and by different reaction rates. In order to obtain high molecular weights the rate of propagation must therefore be considerably higher than that of any of the other reactions.

Step-growth polymerizations are, in general, also characterized by initiation, propagation, and termination reactions. However, both rates and mechanisms of these reactions do usually not differ significantly from each other. Fur-

Table 9. Identification of polymerization mechanism by copolymerization.

Monomer mixture	Polymerization product		
	Cationic	Radical	Anionic
Styrene-methyl methacrylate	Polystyrene	Random copolymer	Poly(methyl methacrylate)
Isobutene-vinyl chloride	Polyisobutylene	Alternating copolymer	—
Isobutene-vinylidene chloride	Polyisobutylene	Alternating copolymer	Poly(vinylidene chloride)

Table 10. Polymerization mechanisms.

Growth classification	Reaction	Initiation	Mechanism scheme
Chain growth	Addition	Radical or ionic	$R^* + M \xrightarrow{M} RM^* \rightarrow RM_n^*$
	Condensation	Ionic	$R^* + MZ \rightarrow (RM^*Z) \rightarrow RM_n^* + nZ$
	Insertion	Heterogeneous pseudoionic	$R-X \xrightarrow{M} RMX \xrightarrow{M} RM_nX$
Step growth	Addition	Nucleophilic	$aAa + Y \rightarrow (aAay) \xrightarrow{bBb} (aAabBby) \begin{cases} \rightarrow aMb + y \\ \rightarrow aMb + ab + y \end{cases}$
	Condensation	and electrophilic	

thermore, it is usually assumed, and has been confirmed in many cases, that the reactivity of the functional groups at the chain ends is independent of the length of the polymer molecule and thus equal to that of the functional groups of the corresponding monomer. Consequently, reaction between monomers can occur with equal ease as reaction between monomer and polymer chains. High molecular weights in this polymerization reaction are therefore obtained only at high monomer conversions. For many cases, interactions between chains entailing linkages that had been formed by reactions of the functional end groups occur readily. Compared to the chain-growth polymerization, the overall rate of polymerization is generally lower in the step-growth process.

It can be easily shown that polyaddition and polycondensation reactions occur within either classification, and that they constitute only a part of the reactions encountered in the formation of polymers. Another important process is the polyinsertion reaction which pertains to polymerization processes characterized by the insertion of monomer between initiator fragments and the growing chain. This insertion is usually preceded by a coordination of the monomer with the initiator.

General schemes of the considered principal reactions in relation to the main growth classifications are shown in Table 10.

Polymer properties, especially constitutional parameters of the polymer structure depend considerably upon the particular polymerization process and may be determined or affected by either the mechanism of initiation or the corresponding termination mechanism. It appears therefore to be in order to point out a few of the reactions entailed in some of the considered mechanisms.

It has been shown that polymerization reactions are usually characterized by initiation, propagation and termination reactions. In practical system, however, a fourth reaction is often encountered. It pertains to a process in which, for instance, in radical polymerization the center of radical reactivity is transferred from the growing chain to another species by an actual exchange of an atom or a group of atoms between the two reactants. This transfer reaction results in the formation of an inert polymer molecule without affecting the radical reactivity of the system. The total process of radical polymerization can thus be represented by the kinetic scheme shown in eqs. (4)–(7).

Since the transfer reaction produces inert polymer, it may be considered a part of the termination process which in turn may then be characterized by any of the three main groups of reactions: unimolecular reactions resulting in loss of radical activity; bimolecular radical-molecule reactions; bimolecular radical-radical reactions.

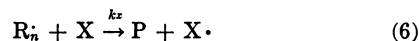
Initiation:



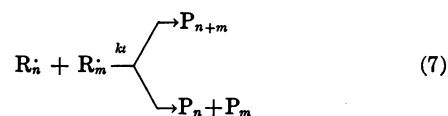
Propagation:



Transfer:



Termination:



The first group pertains to processes in which the growing radical isomerizes to an unreactive form or becomes trapped in solid polymer. The second reaction produces inert polymer and a new free radical, which may or may not be capable of causing further growth. The new radical may be derived from any molecule present in the system, including monomer, solvent, initiator, and inactive polymer. Branching, for instance, may be the result of radical-polymer reactions entailing an active new radical. If the new radical is inactive, then the reaction is referred to as degradative, and depending upon the facility of the reaction, it constitutes either retardation or inhibition.

The third group is the most widely known one, involving two possible mechanisms according to which termination results from mutual destruction of the radical reactivity by a bimolecular reaction between two radicals. The two reactions are known as disproportionation and combination. These termination processes are summarized in Table 11.

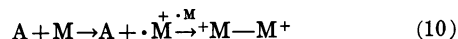
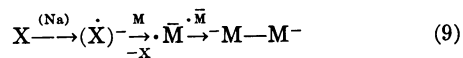
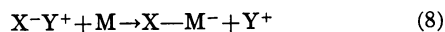
The classical ionic polymerizations are initiated by cations and anions which at the initiation step attach themselves to the monomer [eq. (8)].

Another mode of initiation involves radical ions capable of converting monomer molecules into radical ions by electron transfer. The monomer radical ion then dimerizes and forms a di-ion. [eq. (9)]. Examples for this type of initiation are the polymerization of styrene initiated by naphthalene anions in tetrahydrofuran and anionic polymerizations initiated by ketyls.

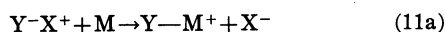
Use of electron acceptors such as aluminum alkyls results in the formation of radical cations upon reaction with the monomer. In this process the electron acceptor is converted to an anion [eq. (10)].

Cationic initiation may also involve the addition of a cation to a monomer molecule [eq. (11a)]. An example is the reaction of boron trifluorohydride with isobutylene [eq. (12)].

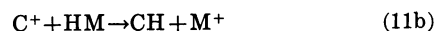
Initiation:



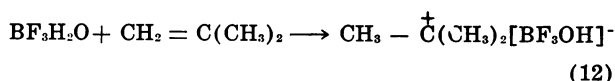
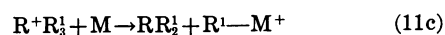
Addition of a cation:



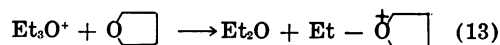
Hydrid abstraction:



Cation transfer:



Hydrid abstractions [eq. (11b)] characterize the initiation by carbonium salts such as $Ph_3C^+[SbCl_6]^-$; cation transfer [eq. (11c)] is involved in the polymerization of tetrahydrofuran [eq. (13)].



Termination reactions in ionic polymerization are given in eqs. (14)–(16).

Reactions (14)–(16) pertain to the anionic polymerization. Termination in cationic polymerizations is assumed to be caused by the initiator. This may entail inactivation of the initiator by its addition to allylic groups formed by proton and hydrid transfer reactions. In addition, isomerizations involving the growing cations and the corresponding counterion have

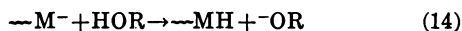
Table 11. Termination processes in radical polymerization.

Reaction type		
First-order termination	Unimolecular	Isomerization Entanglement or agglomeration in impermeable polymer, "trapping"
	Chemical deactivation Physical deactivation	
Second-order termination	Bimolecular	Branching Retardation, inhibition $2R-CH_2-CH_2 \rightarrow R-CH=CH_2 + R-CH_2-C-H_2$ $2R-CH_2-CH_2 \rightarrow R-CH_2-CH_2-CH_2-CH_2-R$
	Nondegradative	
	Degradative	
	Disproportionation Combination	

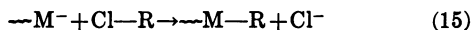
been considered for the formation of inactive ester structures.

General schemes of the reactions entailed in the insertion polymerizations (coordination polymerization) are shown in eqs. (17)–(19).

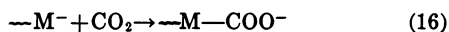
Proton transfer:



Nucleophilic substitution:



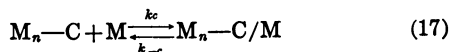
Addition:



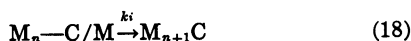
Interaction with initiator:

Formation of allylic groups
Isomerization entailing the counterion

Monomer-catalyst coordination:

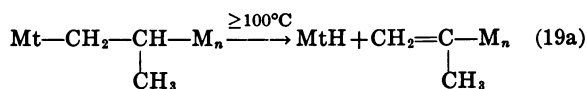


Monomer insertion:



Termination:

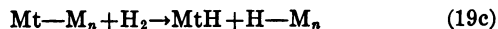
Thermal:



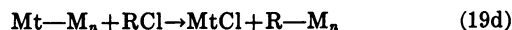
• $ZnEt_2$:



H_2 :



RCl :



The mechanism of the insertion reaction resembles somewhat that which appears to govern enzyme catalyzed reactions. In either case, the molecule undergoing reaction is absorbed reversibly on a specific side of the catalyst (enzyme) to form a stable catalyst-olefin (enzyme-substrate) complex whose subsequent rearrangement (decomposition) is the rate-controlling step. Whereas in this step the enzyme reaction yields the reaction products and regenerates the enzyme, a monomer unit is inserted into the polymer chain and the active catalyst side is regenerated in case of the considered polymerization process, which is schematically shown in eq. (20).

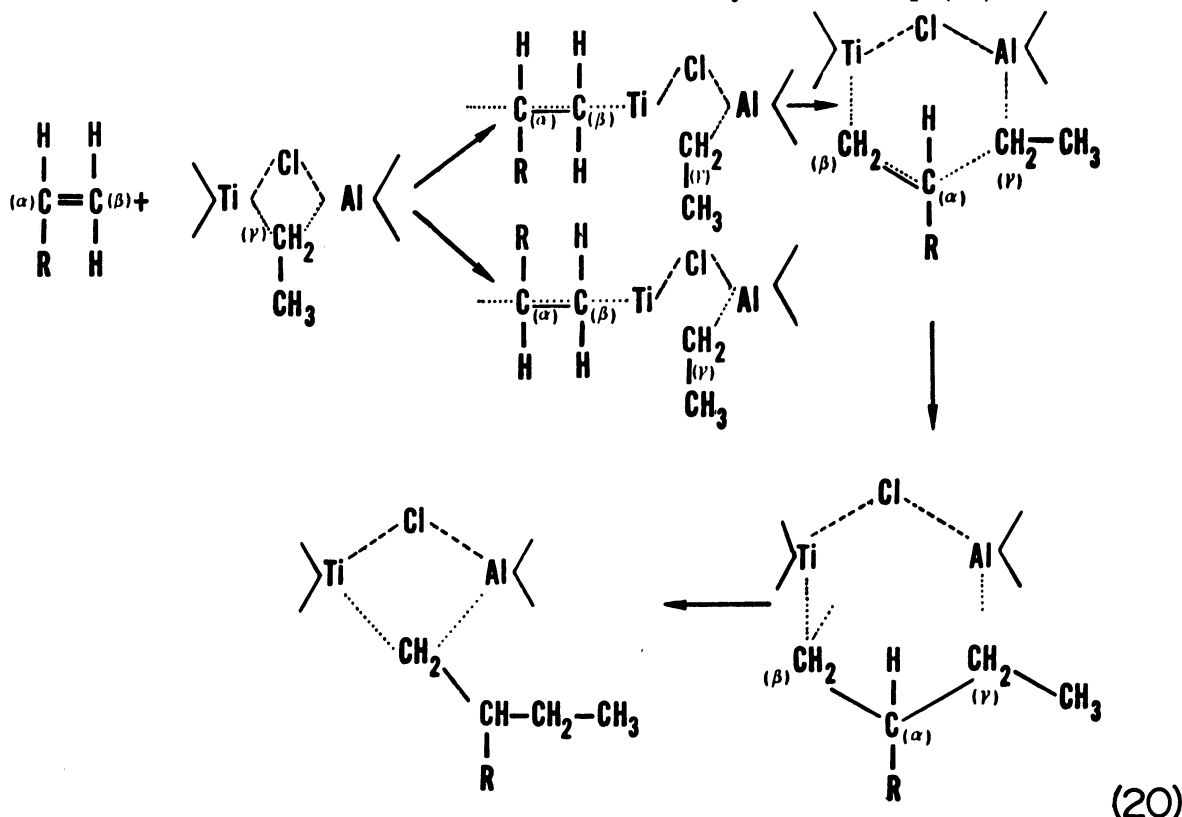


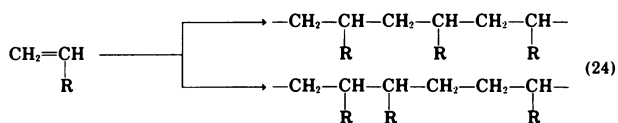
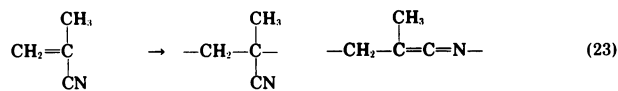
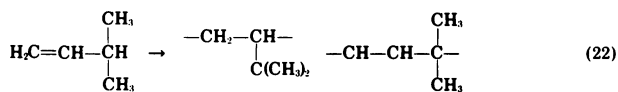
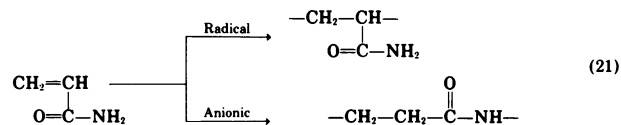
Table 12. Determinants of polymer structures.

Constitution	Interlinking	Polymer chains
	Composition	Repeating units Homopolymers Random, alternating copolymers Block copolymers Graft copolymers
Configuration	Substituents Endgroups Molecular weight	Number-average Weight-average Molecular weight distribution
	Ideal structures Real structures	Isotactic Syndiotactic <i>cis/trans</i> Tacticity Dyads, triads Sequence lengths

This scheme indicates that two steric structures could be formed, but thus far only isotactic polymer has been obtained with this solid catalyst system. It has been assumed that the two possible olefin addition complexes are energetically somewhat different and that accordingly one addition step is favored over the other.

Structure

Both physical and chemical quantities determine the structure of a polymer. They are constitution, configuration, conformation, orientation, and crystallization. The principal structural quantities that are direct consequences of



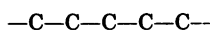
the synthetic approach by which a particular polymer was obtained are constitution and configuration. (Table 12).

Polymer chains may be interlinked to form linear, branched, or crosslinked structures.

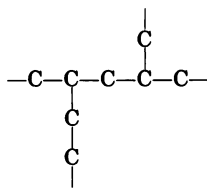
Different types of initiation or isomerization processes may be responsible for the formation of isomeric structures characterized by different modes of interlinking of repeat units as indicated in eqs. (21)–(24).

With respect to composition polymers are divided into homopolymers and copolymers, the latter being subdivided into random, alternating, block, and graft copolymer.

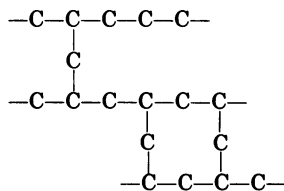
Linear:



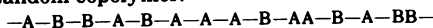
Branched:



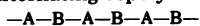
Crosslinked:



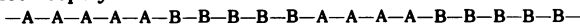
Random copolymer:



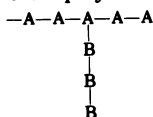
Alternating copolymer:



Block copolymer:

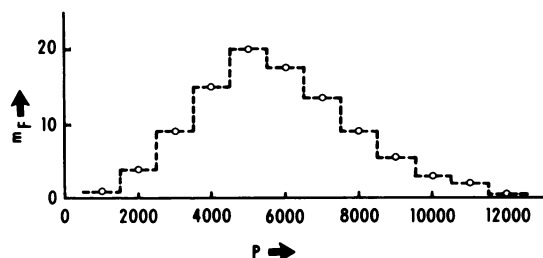


Graft copolymer:



One of the most significant constitutional parameters is the molecular weight. Molecularly uniform macromolecules, that is, molecules of identical molecular weight, are obtained only when certain mechanistic conditions

are satisfied. Most polymerizations, however, are statistical reactions and yield therefore products that are characterized by a more or less broad distribution of their molecular weights. This can be shown by careful fractionation of polymer samples which may yield results of the type shown in Figure 1.



Distribution Step-Diagram, Which Indicates the Fraction (in %) of the Total Product Represented by the Successive Polymer Fractions.

FIGURE 1. Distribution step diagram, which indicates the fraction (in %) of the total product represented by the successive polymer fractions.

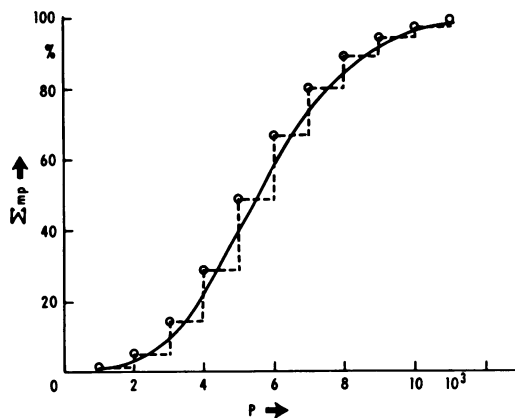
To evaluate results of this type the sum of the fraction ΣM_F is plotted against the degree of polymerization. This results in an integral distribution curve (Fig. 2) from which a differential distribution curve can be readily obtained.

Such a distribution curve provides an accurate description of the polymer with regard to the size of its molecules. Because of this poly-disperse character of most polymers, the molecular weights, determined in one way or another, represent averages. Depending upon the particular method of determination either a number-average or a weight-average molecular weight is obtained. These averages \bar{M}_n , \bar{M}_w are defined as shown in eqs. (25) and (26).

The ratio \bar{M}_w/\bar{M}_n or the value of $(\bar{M}_w/\bar{M}_n - 1)$ provides information on the width of the distribution and thus the uniformity of the molecular weights. A value of $\bar{M}_w/\bar{M}_n = 1$ denotes a molecularly completely uniform polymer.

If the mechanism of polymer formation is known, distribution functions can be calculated and have been derived for polymers obtained by addition and condensation processes, they are known as "normal" or "most probable" distribution. For this type of distribution, values have been obtained for the ratio \bar{M}_w/\bar{M}_n

INTEGRAL DISTRIBUTION CURVE



DIFFERENTIAL DISTRIBUTION CURVE

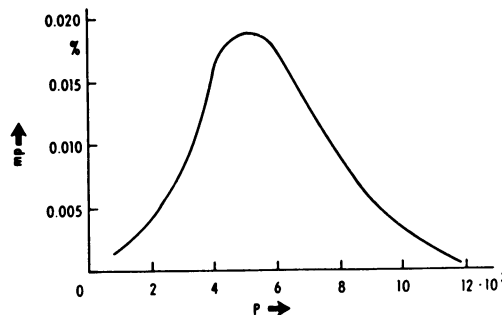


FIGURE 2. Integral and differential distribution curves.

for different polymerization mechanisms as shown in Table 13.

The quantity K is the so-called "degree of coupling" and is equal to the number of chains contained in one polymer molecule.

Table 13. \bar{M}_w/\bar{M}_n as a function of mechanism.

	K	$\frac{\bar{M}_w}{\bar{M}_n} = \frac{K+1}{K}$
Monofunctional initiation	1	2
Difunctional initiation	2	1.5
Unimolecular termination	1	2
Degradative termination	1	2
Disproportionation	1	2
Combination	2	1.5
Multifunctional initiation	n	$1 + 1/n$
Branching	n	$1 + 1/n$

$$\bar{M}_n = M_0 \bar{P}_n + \sum_E M_E \quad (25)$$

where

$$\bar{P}_n = \frac{n_1 P_1 + n_2 P_2 + \cdots n_n P_n}{n_1 + n_2 + \cdots n_n} = \frac{\sum_1^n n_i P_i}{\sum_1^n n_i}$$

$$\bar{M}_w = M_0 \bar{P}_w + \sum_E M_E$$

where

$$\bar{P}_w = \frac{w_1 P_1 + w_2 P_2 + \cdots w_n P_n}{w_1 + w_2 + \cdots w_n} = \frac{\sum_1^n w_i P_i}{\sum_1^n w_i}$$

Here M_0 is the formula weight of repeating unit and M_E the formula weights of endgroups, n and w are the number and weight fractions, respectively of polymer molecules of molecular weight M .

Configurational aspects in polymer chemistry are concerned mainly with the position of substituents on central chain atoms relative to the neighboring structural unit. If the two neighboring central chain atoms are both carbon atoms, then the configuration of this dyad is determined by the position of the substituents relative to the bond between the two central chain atoms. By convention a definition is used which may be explained with the aid of Figure 3.

If the size of the three substituents, r , R , and \sim (chain) increases counterclockwise, then the bond to this central atom may be denoted a $(+)$ bond, consequently the bond from this atom to the next chain atom is then a $(-)$ bond. When the considered substituents are arranged clockwise then the bond to the central atom is the $(-)$ bond the bond from this atom to the chain the $(+)$ bond. Two central atoms or the structural units to which they belong have identical configuration if the corresponding bonds are characterized by the same set of $(+)$ and $(-)$ notations. Polymers in which all central chain atoms have the same

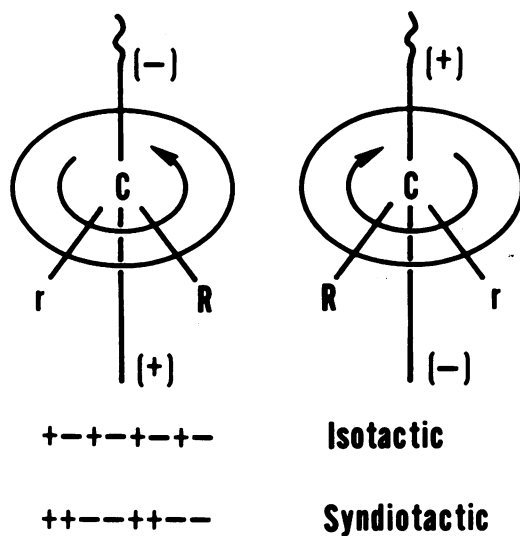


FIGURE 3. Definition of configuration.

configuration are defined as isotactic. These polymers are thus characterized by alternating $(+)$ and $(-)$ bonds between the chain elements. If, however, each second central chain atom has the opposite configuration then the polymer is called syndiotactic. Figure 4 shows projections of an isotactic and syndiotactic chain segment of a polymer of the general structure $-(CH_2-CRr)-$.

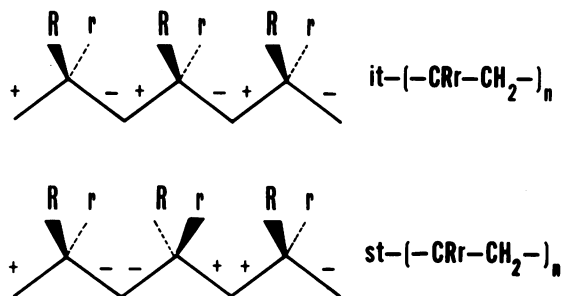
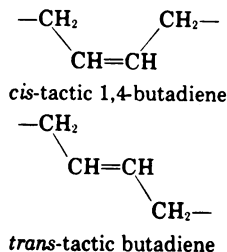


FIGURE 4. Projection of isotactic (it) and syndiotactic (st) chain segments.

Polymers containing double bonds in the polymer chain may exist in *cis*-tactic and *trans*-tactic configuration, as shown for 1,4-butadiene:



Polymers with one stereoisomeric center per structural unit are called monotactic, those with two or three are consequently called ditactic and tritactic. Both the isotactic and syndiotactic structures are ideal structures and require an infinite long chain and a complete absence of configurational defects. Real polymers are however characterized by finite chain length (and consequently endgroups), and by less than perfect steric arrangements. Their characterization is therefore concerned with the average arrangement and order of the stereoisomeric centers. The smallest unit consists of two stereoisomeric centers and is called a dyad, which may be either isotactic or syndiotactic. The identification of the steric structure of the dyad does not provide adequate information on the prevailing tacticity of the entire polymer. As indicated in Figure 5, a block copolymer consisting of both an isotactic and an

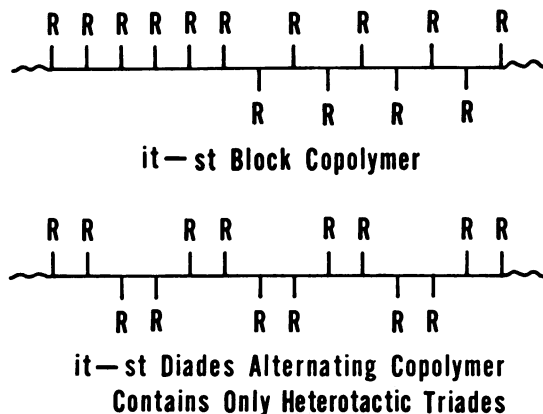


FIGURE 5. Arrangement and order of stereoisomeric centers.

syndiotactic block, each of very high molecular weight, would have the same number of isotactic and syndiotactic linkages as a polymer with alternating isotactic and syndiotactic dyads. To describe the "real" structure of a polymer, therefore, a sequence of at least three stereoisomeric centers (triads) is necessary. They are called isotactic, syndiotactic, and heterotactic. Introduction of the triads permits a description of the gross configuration of a particular polymer and also an estimation of the length of all isotactic and syndiotactic sequences.